



Electrochemical removal of NO_x using oxide-based electrodes - A review

Kammer Hansen, Kent

Published in:
International Journal of Electrochemical Science

Link to article, DOI:
[10.20964/2018.10.09](https://doi.org/10.20964/2018.10.09)

Publication date:
2018

Document Version
Publisher's PDF, also known as Version of record

[Link back to DTU Orbit](#)

Citation (APA):
Kammer Hansen, K. (2018). Electrochemical removal of NO_x using oxide-based electrodes - A review. *International Journal of Electrochemical Science*, 13(10), 9273-9280. <https://doi.org/10.20964/2018.10.09>

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Mini Review

Electrochemical Removal of NO_x Using Oxide-Based Electrodes – A Review.

K. Kammer Hansen

Department of Energy Conversion and Storage
Technical University of Denmark – DK-4000, Roskilde, Denmark

*E-mail: kkha@dtu.dk

Received: 1 June 2018 / Accepted: 28 June 2018 / Published: 1 September 2018

Solid-state electrochemical reduction of NO_x using oxide-based electrodes is reviewed. Different types of electrode and cell geometries have been used in the literature. Using simple ceramic point electrodes prepared using different materials; it has been shown that nitric oxide is reduced at different rates on different materials. For perovskites, it has been shown that the amount of trivalent transition metal and amount of oxide ion vacancies are important for the reduction of nitric oxide. The same applies to Cu and Ni-based K₂NiF₄ structures. For spinels, the pattern is less clear, but they are all able to reduce nitric oxide. Current densities are much higher when reducing nitrogen dioxide compared with nitric oxide on both perovskites and spinels. In gas mixtures containing nitric oxide and oxygen, the addition of BaO leads to fairly high conversion of nitric oxide into nitrogen. Finally, it has been shown that oxidizing nitric oxide to nitrogen dioxide before reducing to nitrogen is very beneficial, leading to current efficiencies of up to 65%.

Keywords: Electrochemical deNO_x, NO, NO₂, Oxides

1. INTRODUCTION

Electrochemical removal of NO_x in an all solid-state cell is a spin off from solid oxide fuel cell (SOFC) technology. It is a minor research field within solid-state electrochemistry. The idea is to reduce the NO_x at the cathode in a solid-state cell based on an oxide ionic conductor. When a potential is applied to the cell, the NO_x is reduced at the cathode to nitrogen and oxide anions, which are transported through the electrolyte to the anode, where oxygen is formed. Such a concept has several advantages in comparison with commercially available technologies such as selective catalytic reduction (SCR) and the concept of NO_x storage and reduction (NSR). Compared to SCR technology, there is no need to add a reducing agent, as current is directly used to reduce the NO_x. This eliminates

the need to store urea on a vehicle and reduces the risk of urea slip. In comparison with NSR technology, the need to operate an engine at fuel-rich conditions for shorter intervals is eliminated, thereby making sophisticated engine control unnecessary.

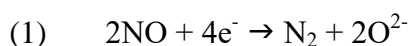
Several issues have to be addressed before electrochemical reduction of NO_x can become a durable solution. First, the operating temperature has to be lowered down to 200 °C. As the technology is based on a spin off from SOFC technology operating at much higher temperatures than the exhaust temperature of a diesel engine, this is not an easy task. Second, the power consumption has to be lowered. As the reduction of oxygen is a competing reaction at the cathode, there is a need for a NO_x selective electrode.

This review covers the available literature regarding electrochemical reduction of NO_x in an all solid-state cell based on an oxide ionic conductor and oxide-based electrodes. For other types of electrodes, see [1, 2].

First, some basic considerations will be given, and then, a literature survey will be undertaken. Based on this, a conclusion will be given.

2. SIMPLE CONSIDERATIONS REGARDING ELECTROCHEMICAL REDUCTION NO_x:

The electrochemical reduction of nitric oxide can be written as:



By the use of Factsage, the potential for the reduction of nitric oxide to oxygen and nitrogen at 400 °C vs. air can be calculated. This gives a value of 0.38 V vs. air. This implies that in principle by adjusting the applied voltage, the reduction of nitric oxide can be initiated at a higher potential than the reduction of oxygen. However, as oxygen evolution and oxidation of nitric oxide to nitrogen dioxide are also possible these two processes inhibit the reduction of nitric oxide. Therefore, the open circuit potential in a cell containing oxygen and nitric oxide is a mixed potential determined by all three processes.

When evaluating the power consumption of an electrochemical cell, the following equation should be noted:

$$(2) \quad P = U \cdot I$$

This is important to note, as it shows that the power consumption can be lowered by decreasing both the applied potential and the current, i.e., by increasing the current efficiency (selectivity).

Simple calculations can give insight into the possibilities for electrochemical removal of NO_x.

A small Peugeot 206 HDI with a 1.4 l engine gives the following requirements:

- 1.4 l diesel engine, 4000 rpm, 250 ppm NO_x
- Area (current density 2.5 mA/cm², current efficiency 20%):
– 20 m², 500 cells, (20*20 cm²), length: 25 cm
- CGO10 conductivity at 200 °C: 10⁻⁵ S/cm
- Current density: 2.5 mA/cm²
- Thickness of electrolyte: 10 μm

- Voltage drop: 0.25 V
- Current density: 2.5 mA/cm²
- Voltage drop: 1.25 V
- ASR: 500 Ωcm²
- From literature: 750 Ωcm² (estimated) at OCV at 200 °C [3]
- Sr_{0.95}Ag_{0.05}Nb_{0.1}Co_{0.9}O_{3-d}
- Lower ASR at polarization and for NO₂

These simple calculations clearly reveal that electrochemical deNO_x is a practical possibility even at low temperatures. If the values given here can be demonstrated, electrochemical deNO_x can even compete with the state-of-art SCR technology.

3. LITERATURE REVIEW:

Early work: The first ever study of electrochemical reduction of nitric oxide was published in 1975 by Pancharatnam et al. [4]. It was shown that nitric oxide can be reduced to nitrogen and oxide anions by the use of porous platinum or gold electrodes on a scandium stabilized zirconia electrolyte in the absence of oxygen in the temperature interval 600 – 800 °C. A peculiar effect was observed when potentials below -2.2 V vs. air were applied to the cell. Here, the reduction of nitric oxide was many times higher than the Faradaic value. It was suggested that this was due to the formation of color centers on the zirconia surface, i.e., the reduction of nitric oxide occurred on the surface of the zirconia electrolyte and not on the electrode. This was later confirmed [5].

Several studies using noble metal-based electrodes have been undertaken, see [1, 2] for a review. The rest of this review covers the open literature for NO_x removal using oxide-based electrodes.

Model electrode studies: A simplified approach to study the electrochemical reduction of NO_x is to use model electrodes that are based on cone-shaped electrodes pressed towards the solid electrolyte. This approach has been extensively used by the group at DTU. This technique is used in conjunction with cyclic voltammetry. Four classes of ceramic electrodes have been studied by this method: perovskites, spinels, fluorites and K₂NiF₄ structures.

Perovskites: In a series of four papers, base perovskites based on Cr, Mn, Fe and Co were studied [6, 7, 8, 9]. By varying the La/Sr ratio and measuring activity in atmospheres containing either nitric oxide or oxygen, the properties needed for the materials to reduce either nitric oxide or oxygen were determined. It was suggested that the activity of Sr and V substituted lanthanum chromites towards reduction of nitric oxide was determined by the amount of oxide ion vacancies, electronic conductivity and perhaps the amount of Cr(III). For the LSM and LSF based perovskites, it was shown that activity towards reduction of nitric oxide was due to the amount of trivalent transition metal ions and oxide ion vacancies. For the cobaltites, the same was valid with the exception that for the strontium rich cobaltite, the mobility of the oxide ions also played a role.

The mixed perovskites between manganese and iron (LSFM) were also studied [10]. A new concept was introduced to explain the activity of these perovskites for the reduction of nitric oxide and

the redox capacity. It was shown by thermogravimetry that compounds showing a large variation in oxygen stoichiometry (that is, average valence state of the transition metals) with a change in oxygen partial pressure exhibit the highest activity towards reduction of nitric oxide. It is, therefore, suggested that a perovskite compound needs to be redox active to reduce nitric oxide at a high rate.

A-site deficient perovskites have also been studied [11]. The series $(\text{Pr}_{0.6}\text{Sr}_{0.4})_{1-s}\text{Fe}_{0.8}\text{Co}_{0.8}\text{Co}_{0.2}\text{O}_{3-d}$, with s equal to 0.01, 0.05, 0.10, 0.15, 0.20 and 0.25, was investigated as cathodes for the electrochemical reduction of nitric oxide and oxygen. It was shown that the activity in an oxygen-containing atmosphere decreased with increasing A-site deficiency. This was suggested to be due to loss of cobalt from the perovskite phase.

Lately LSM perovskites were reinvestigated [12]. Three different compositions were studied; one without strontium, one with 15% strontium and one with 50% strontium. Before recording the voltammograms, the electrodes were polarized at 0.4 V vs. air for 16 h. It was shown that when strontium was present the electrodes activated significantly in the nitric oxide containing atmosphere. In oxygen containing atmosphere the electrodes were slightly deactivated. This was thought to be due to segregation of strontium to the surface of the electrodes during anodic polarization. Strontium is an alkaline earth nitrate with ability to store the NO_x, see later. This could be the reason for the increased performance of the anodically treated electrodes.

K₂NiF₄ structures: In the first of two papers, the electrochemical reduction of nitric oxide and oxygen was studied for $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ -based electrodes [13]. In general, it was shown that the activity towards nitric oxide and oxygen reduction decreased with increasing strontium doping. The highest apparent selectivity was found for the strontium-free compound La_2CuO_4 .

In the second paper, $\text{La}_{2-x}\text{Sr}_x\text{NiO}_4$ -based electrodes were investigated [14]. It was shown that LaSrNiO_4 had the highest apparent selectivity. It was suggested that this was due to a high amount of oxide ion vacancies and the redox pair $\text{Ni}^{2+}/\text{Ni}^{3+}$.

Spinel: In the first of a series of four papers dealing with the reduction of nitric oxide and oxygen on spinel-based oxides, four different spinels were investigated [15]. The four spinels had the compositions, NiFe_2O_4 , CuFe_2O_4 , CoFe_2O_4 and Co_3O_4 . The Cu-containing spinel showed the highest apparent selectivity towards reduction of nitric oxide. The Ni-containing spinel also showed a higher activity towards reduction of nitric oxide compared to oxygen, whereas the spinels containing cobalt were more active towards oxygen reduction than towards the reduction of nitric oxide.

Solid solutions of NiFe_2O_4 and MgFe_2O_4 were also investigated as cathodes for the electrochemical reduction of nitric oxide and oxygen [16]. NiFe_2O_4 showed a relatively high activity in both nitric oxide and oxygen containing atmospheres (in contrast to the previous study); however, MgFe_2O_4 showed a much higher activity in the nitric oxide containing atmosphere than in the oxygen-containing atmosphere.

In an unpublished work by Bræstrup and Hansen, the activity of the two spinels ZnFe_2O_4 and MgFe_2O_4 towards the reduction of nitric oxide was studied. It was shown that the inverse spinel MgFe_2O_4 , with part of the iron(III) on the A-site, was much better at reducing nitric oxide than the normal spinel ZnFe_2O_4 , with no iron(III) on the A-site. This indicates that tetrahedral coordinated iron(III) is very good at reducing nitric oxide compared to octahedral-coordinated iron(III). On the other hand, ZnFe_2O_4 was much better at oxidizing nitric oxide than MgFe_2O_4 .

Another series of spinels, $\text{NiCr}_x\text{Fe}_{2-x}\text{O}_4$, was also investigated for the reduction of nitric oxide and oxygen [17]. Here, the end member NiCr_2O_4 showed a much higher activity in the nitric oxide containing atmosphere than in the oxygen-containing atmosphere, indicating a possible electrode material for the reduction of nitric oxide under net oxidizing conditions. Activity, however, decreased with increasing chromium content.

A final study of spinels as cathode materials for electrochemical deNO_x was likewise done by Bræstrup and Hansen [18]. The series $\text{MgMn}_x\text{Fe}_{2-x}\text{O}_4$ ($x = 0.0, 0.2, 0.4, 0.6, 0.8$ and 1.0) was synthesized and studied by the use of cone-shaped electrodes and cyclic voltammetry. It was shown that in most cases, Mn doping increased the current ratio between nitric oxide and oxygen but lowered the current density.

Fluorites: Only one study for fluorites has been reported in the open literature [19]. A series of praseodymium-doped cerium oxides were studied using cone-shaped electrodes and cyclic voltammetry. It was concluded that the current density in both nitric oxide and oxygen containing atmospheres increased with increasing Pr content up till the maximum doping level of 40% studied. The apparent selectivity was highest for CeO_2 with 10 and 20% Pr-doping. It was observed that the apparent selectivity increased with decreasing temperature.

Different cell structures: Three different cell structures have been investigated: symmetrical cells, with identical electrodes on both sides of a thick dense electrolyte foil, porous cell stacks with alternating thin porous layers for the electrode and electrolyte and tubular cells.

Symmetrical cells: An elegant study was done by Shao and Kammer [20]. Symmetrical electrolyte supported cells with LSM/CGO electrodes were modified by either adding an adsorption layer containing Ba and Pt to the top of the LSM/CGO electrode or by infiltrating the LSM/CGO electrode with $\text{Ba}(\text{NO}_3)_2$. It was shown that the performance of the cells with the two different modifications were similar. This is a very important result, as it shows that there is no need for a complicated multi-layered electrode structure: a simple single-layer electrode structure containing infiltrated Ba is equally good.

A study by another group also used BaO as storage material, but instead used $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-d}$ (LSCF) as the electronic conducting phase [21]. BaO was infiltrated together with Pt. However, no formation of nitrogen was observed in the presence of oxygen.

Recently another study was undertaken [22]. Here LSM/CGO was used as an electrode, but the BaO was co-infiltrated with Pt. In addition to this the effect of adding a reducing agent (propene) was studied. It was shown that co-infiltration of BaO and Pt the catalytic activity towards nitric oxide reduction with propene was enhanced. However, almost no effect of applied potential was observed. This shows that there is almost no coupling between the reduction of nitric oxide with propene and the electrochemical reduction of nitric oxide, i.e. the reaction between propene and nitric oxide cannot be enhanced electrochemically on this type of materials.

Porous cell stacks: A novel concept was suggested in 2010 by the group at DTU [23]. A multi-layered reactor, constructed from alternating layers of porous electrodes and electrolytes, was put forward. The concept was called a porous cell stack. The reactor consists of 11 layers of electrode and electrolyte, corresponding to 5 cells in series. The reactor concept has several advantages: it is self-

supporting, i.e., there are no supporting layers taking up un-necessary space, and it contains a large electrode area in a small unit of volume.

A porous cell stack consisting of a LSM/CGO composite electrode and a CGO electrode was tested for removal of NO [23]. It was shown that the porous cell stack can remove nitric oxide in the absence of oxygen. When oxygen was added, no reduction of nitric oxide was observed. The porous cell stack was infiltrated with different cerium oxide-based compounds, which improved the activity of the porous cell stacks towards the reduction of nitric oxide. Infiltration with CGO made the removal of nitric oxide possible in the presence of oxygen, even though the conversion was very low (1%) with a current efficiency of 2%.

A porous cell stack consisting of LSF/CGO electrodes and CGO electrolytes was infiltrated with potassium nitrate or oxide [24]. This did alter (increase) the conversion of nitric oxide into nitrogen when no oxygen was present. However, upon introduction of oxygen into the reaction mixture, no nitrogen formation was detected during polarization.

Later, the group at DTU improved the porous cell stack concept by infiltration with an alkaline earth nitrate, $\text{Ba}(\text{NO}_2)_3$ [25]. In this case, a significant conversion of nitric oxide was observed under net oxidizing conditions. The current efficiency was of the order of 11% for an 11-layer cell stack (5 cells in series), corresponding to an actual current efficiency of 2.2%. This concept was further improved by the group at DTU by adding small amounts of Co to the B-site of the LSM [26]. In two papers, the current efficiency was first increased to 20% [26] and then up to 32% (for an 11-layer cell stack, corresponding to an actual current efficiency of 6.4%) [27]. This is among the highest current efficiencies ever reported for a full ceramic cell, without the use of noble metals. The role of cobalt is probably to assist in the formation of nitrogen dioxide – an intermediate in the formation of nitrates. Cobalt is a better oxidation catalyst compared to manganese. The micrographs also reveal the difference in using LSM and LSCF. When using LSM, BaO particles are clearly visible in the micrographs [27]. However, when using LSCF, no BaO particles are observed in the micrographs [22]. The reason for the difference could be the following: cobalt has a higher ability to form K_2NiF_4 structures than manganese; BaO might then have reacted with the cobalt-based perovskite phase during heat treatment forming a new phase, leaving no BaO behind for storage of NO_x.

Porous cell stacks with LSF/CGO electrodes has also been used together with infiltration of different un- and doped-cerium oxides [28]. When propene and nitric oxide was fed to the reactor together with oxygen, the conversion of nitric oxide into nitrogen was enhanced, when the porous cell stack was infiltrated with cerium based oxides. No enhanced of the reduction reaction was observed when a potential was applied.

Finally porous cell stacks with LSM/CGO electrodes doped with Co was infiltrated with Pt [29]. When the porous cells stacks was left as prepared (no Pt), no effect on reduction of nitric oxide was observed at OCV or upon polarization. In contrast to this when the porous cell stacks was infiltrated with Pt, nitric oxide could be remove both in absence or presence of propene under net oxidizing conditions. Electrochemical promotion was even observed on the Pt infiltrated porous cell stacks. This implies that pure oxides has a very limited ability to reduce nitric oxide electrochemically under net oxidizing conditions.

Tubular cells:

Two examples of the use of tubular cell configurations have been given in the literature. In the first example, LSM/CGO electrodes was used together with a dense CGO electrolyte [30]. When the cells were infiltrated with KNO_3 a high activity towards the reduction of nitric oxide was observed under net oxidizing conditions, even below 300 °C. Again this shows that when adding a storage compound to the electrodes nitric oxide can be reduced under net oxidizing conditions at a high rate.

In the second example similar materials as in [30] was used, but no oxygen was added [31]. No storage compound was added, but the cells could decompose nitric oxide in the absence of oxygen.

Electrochemical reduction of nitrogen dioxide:

Several examples for electrochemical reduction of nitrogen dioxide are given in the literature [16, 17, 18,32]. The studies all use model electrodes. A study of strontium-substituted lanthanum ferrites showed the following: very high current densities of 122 mAcm^{-2} were realized for the most active compound, LSF25, at 400 °C [32]. It was suggested that the amount of oxide ion vacancies and Fe(III) is important for the reduction of nitrogen dioxide for these type of compounds. However, no gas analysis was carried out, and the experience from our laboratory indicates that nitrogen dioxide is reduced only to nitric oxide on perovskites when no storage compound is present in the electrode. On spinels, the reduction of nitrogen oxide is must faster compared to the reduction of nitric oxide.

However, gas analysis was performed by Shao et al. in a recent study. Here, a diesel oxidation catalyst was mounted before an electrochemical reactor, thereby oxidizing nitric oxide to nitrogen dioxide before entering the electrochemical reactor [33]. Record high current efficiencies were found, up to 65%.

On symmetrical cells with LSM/CGO electrodes infiltrated with BaO the reduction of nitrogen dioxide is also must faster than the reduction of nitric oxide [34]. Shao et al showed that when adding an oxidation catalyst, before the flue gas entered the electrochemical reactor, current efficiencies of up to 35% could be achieved.

This indicates that electrochemical reduction of nitrogen dioxide might be a feasible route for NO_x reduction under net oxidizing conditions, when combined with a NO_x storage compound. It also strongly indicates that the oxidation of nitric oxide to nitrogen dioxide is a rate limiting step when using a storage compound.

4. CONCLUSION

The electrochemical reduction of NO_x has been reviewed. It was shown that nitric oxide can be reduced on different oxide-based materials. For perovskites, the amount of oxide vacancies, redox capacity and amount of trivalent transition metal is important. For spinels, no clear pattern was observed. Addition of BaO to the electrodes leads to much higher conversion of nitric oxide into nitrogen.

References

1. K. Kammer, *Appl. Catal. B Environ.*, 58 (2005) 33.
2. K.K. Hansen, *Appl. Catal. B Environ.*, 100 (2010) 427.

3. Yi. Zhu, W. Zhou, R. Ran, Y. Chen, Z. Shao and M. Liu, *Nano Lett.*, 16 (2016) 512.
4. S. Pancharatnam, R.A. Huggins, and D.M. Mason, *J. Electrochem. Soc.*, 122 (1975) 869.
5. T. M. Gür and R.A. Huggins, *J. Electrochem. Soc.*, 126 (1979) 1067.
6. K. Kammer Hansen, *Mater. Res. Bull.*, 48 (2013) 3274.
7. K. Kammer Hansen, *J. Electrochem. Soc.*, 160 (2013) F1254.
8. K.K. Hansen, *Electrocatalysis*, 5 (2014) 256.
9. K.K. Hansen, *J. Electrochem. Soc.*, 157 (2010) P79.
10. K. Kammer, E. M. Skou, *Solid State Ionics*, 176 (2005) 915.
11. K. Kammer Hansen, *J. Mater. Sci.*, 46 (2011) 6457.
12. K. Kammer Hansen, *Int. J. Electrochem. Sci.*, 13 (2018) 4782
13. V.L.E. Simonsen, L. Nørskov, and K.K. Hansen, *J. Solid State Electrochem.*, 12 (2008) 1573.
14. V.L.E. Simonsen, L. Nørskov, A. Hagen, and K. Kammer Hansen, *J. Solid State Electrochem.*, 13 (2008) 1529.
15. V.L.E. Simonsen, D. Find, M. Lilliedal, R. Petersen, and K. Kammer, *Topics in Catalysis*, 45 (2007) 143.
16. F. Bræstrup and K.K. Hansen, *J. Solid State Electrochem.*, 13 (2009) 1241.
17. F. Bræstrup and K.K. Hansen, *J. Solid State Electrochem.*, 14 (2009) 157.
18. F. Bræstrup and K.K. Hansen, *J. Appl. Electrochem.*, 39 (2009) 2369.
19. R.M.L. Werchmeister and K.K. Hansen, *Electrochim. Acta*, 114 (2013) 474.
20. J. Shao and K.K. Hansen, *J. Mater. Chem. a*, 1 (2013) 7137.
21. X. Wang, A. Westermann, Y.X Shi, N.S. Cai, M. Rieu, J.-P. Viricelle, P. Vernoux, *Catalysts*, 7 (2017) 61.
22. A.Z. Friedberg and K. Kammer Hansen, *J. Electrochem. Sci. Eng.*, 7(4) (2017) 153
23. R.M.L. Werchmeister, K.K. Hansen, and M. Mogensen, *Mater. Res. Bull.*, 45 (2010) 1554.
24. M.L. Traulsen, F. Bræstrup, and K. Kammer Hansen, *J. Solid State Electrochem.*, 16 (2012) 2651.
25. M.L. Traulsen, K.B. Andersen, and K.K. Hansen, *J. Mater. Chem.*, 22 (2012) 11792.
26. R.M.L. Werchmeister, J.J. Bentzen, K.B. Andersen, and K. Kammer Hansen, *J. Electrochem. Soc.*, 161 (2014) H663.
27. A.Z. Friedberg and K.K. Hansen, *J. Solid State Electrochem.*, 19 (2015) 1611.
28. A.Z. Friedberg and K.K. Hansen, *J. New Materials Electrochem. Systems*, 18 (2015) 111
29. A.Z. Friedberg and K. Kammer Hansen, *J. Electroceram.*, accepted (2018)
30. K. Hamamoto, T. Suzuki, Y. Fujishiro, M. Awano, *J. Electrochem. Soc.*, 158 (2011) B1050
31. Y. Tong, B. Zhao, T. Yang, F. Yang, Q. Hu, C. Zhao, *Int. J. Electrochem. Sci.*, 10 (2015) 5338
32. K. K. Hansen, *Electrochem. commun.*, 9 (2007) 2721.
33. J. Shao, Y. Tao, and K.K. Hansen, *Electrochem. commun.*, 72 (2016) 36.
34. J. Shao, Y. Liu, Q. Cheng, W.-J. Zhang, Y. Tao and K. Kammer Hansen, *J. Electrochem. Soc.*, accepted